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"A METHOD OF MAKING A SENSOR FOR MULTI ION SENSITIVE ELECTRODE AND VOLTAMMETRIC APPLICATIONS AND THE SENSOR SO MADE".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi 110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

This is an invention by Gollakota Prabhakar Rao, Navin Chandra and Ganesa Ganapadigal Subramanian, all of Central Electrochemical Research Institute, Karaikudi.

This invention relates to the method marking graphite substrate sensor for use as ion-sensitive electrode as well as voltammetric electrode.

Hitherto it has been proposed to measure concentrations/activities of ions present in solution by a number of known electrochemical methods including potentimetric methods which are direct and simple. The applicability of potentimetric methods using conventional electrodes is restircted by factors such s nonavailability of suitable indicator electrode and/or the succeptibility of indicator electorde to oxidation in several cases. With the advent of ion-sensitive electrodes for various ions, it has now become possible to use potentiometric methou of analysis in redox media also. These ion sensitive electrodes depending on the material of construction of the membrane, can be used only for monitoring the ions to which they are sensitive and a completely different ion-sensitive electrode is required for monitoring respective individual ion. The graphite substrate sensor electrode of the present invention can however be used to monitor various ionic species in solution simply by activating the oter graphite membrane surface with appropriate sensitizing material. A second application of the graphite substrate sensor of the present invention is as working electrode in voltammetry for which purpose the graphite membrane surface is polished with fine emery and used as such with no sensitizing material applied.

The preparation of the graphite substrate sensor broadly involves making a substantially impervious pellet by compression of a homogenized mixture of pure graphite powder with an inert binder and incorporation of the pellet so obtained in a suitable holder after providing proper electrical contact.

The object of the invention is therefore to work out the details of the procedure for making the graphite substrate sensor membrane and assemble electrodes using these membranes which when sesitized with active material would give steady and stable potentials, in solutions containing corresponding ions in solution and which can be used as voltammetric electrode.

For preparation of the membrane, 0.8 to 1.0 gramme of highly pure graphite powder is mixed througly with 0.2 to 0.3 gramme of room temperature curing silicone binder to obtain a homogeneous mixture and the mixture is compressed in a die at 3.0 to 4.5 tons/cm^2 for 20-30 minutes. The membranes so obtained (6-8 mm thick) are mounted in a 15 cms length and 10 mm inner diameter hollow glass tubes with the help of an epoxy or moulded copper wire is fixed to the inner surface of the graphite membrane for providing electrical contact with the help of a conducting epoxy.

For using this electrode as ion-sensitive electrode, the outer surface of the graphite membrane was polished with 2/0 fine emery paper and after washing with water, a thin coating of active material, sensitive to the ion to be estimated in solution (e.g. CuS-Ag_2S for Cu^{2+} ions or Ag_2S - AgI for I^- ions etc.) was mechanically applied. After washing, the electrode was immersed

inthe solution of the ion of interest. The potential of the electrode was recorded against a standard reference electrode such as Ag/AgCl electrode on a pH/mV meter having a sensitivity of ± 0.1 mV. The potential of the electrode was found to bear a Nernstian relationship with concentration of ion being detected in solution Potential vs log concentration plots are indicated in accompanying drawings. Sheet no.1 rolates the potential vs log concentration plots for ion selective measurement in 0.5 M $NaNO_3$ background.

1. Iodide 2. Bromide 3. Chloride
3. Thiocyanate 5. Lead 6. Cupric
7. Mercuric 8. Silver

The line has a slope value of RT/ZF where 'Z' is the valency of the ion being estimated; R,T and F have their usual meaning.

Similarly, for voltammetric applicaions, the electrode was polished with 5/0 emery paper and linear sweep voltammograms were recorded in ferricyanide solutions in 1.0M KCl background.

The following examples illustrate the various details for making the graphite substrate sensor.

Example-1

0.8 gramma of pure graphite powder was throughly mixed with 0.2 gramme of room temperature curing silicone polymer in an agate mortar and the homogenized paste was compressed in a die at 4.5 tons/cm^2 pressure for 20 minutes to obtain substantially imprevious 10 mm diameter graphite pellet. The pellet was

incorporated in a glass sleeve with the help of epoxy adhesive after fixing a shielded copper wiere to the inner side of the graphite membrane with a conducting epoxy.

(a) As ion-sensitive electrode

For ion-sensitive applications, the response of the electrode was measured for silver, cupric, iodide and thiocyanate ions in sample solutions. The experimental details are given below;

The electrode was washed several times with double distilled water after polishing the outer graphite membrane surface with 2/0 fine emery paper and Ag_2S powder was rubbed over the surface. To remove loose powder particles, the electrode was polished gently on a plane paper and washed with double distilled water. The electrode was then immersed in solutions containing silver ions in the concentration range 10^{-6} kto 10^{-1} M in 0.5 M $NaNO_3$ background and the potential of the electrode was noted down against a doubleenjunction Ag/AgCl reference electrode. The results are given below in Table -1.

Table-1

Concentration of Ag^+ ion in solution (M)	Electrode potential (mv) vs. Ag/AgCl reference electrode
10^{-6}	235.9
10^{-5}	296.8
10^{-4}	354.3
10^{-3}	414.4
10^{-2}	473.4
10^{-1}	532.3

The Ag_2S precipitate was removed from the membrane surface by polishing with 2/0 emery paper and Ag_2S - CuS composite was applied on to the membrane surface following the procedure given earlier. The loose particles of the active material were removed by gently polishing the membrane surface on a plane paper and washin under a jet of double distilled water. The electrode was then tested for its response to Cu^{2+} ions in solution in the concentration range 10^{-6} to 10^{-1} M in 0.5 M $NaNO_3$ background. The results are given in Table 2.

Table-2

Concentration of Cu^{2+} ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	216.3
10^{-5}	224.5
10^{-4}	245.5
10^{-3}	272.2
10^{-2}	300.9
10^{-1}	328.2

The CuS-Ag_2S composite was removed from the membrane surface by polishing and Ag_2S-AgI composite was applied to the membrane surface following the procedure given earlier. After removing loose precipitate and washing with double distilled water, its response was measured in solutions of iodide ions in the concentration range 10^{-6} to 10^{-1} M in 0.5 M $NaNO_3$ background. The potential of the electrode in corresponding iodide ion

solutions is given in Table 3.

Table-3

Concentration of I^- ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	15.3
10^{-5}	-30.0
10^{-4}	-94.4
10^{-3}	-157.9
10^{-2}	-217.0
10^{-1}	-277.1

Following the procedure given above the Ag_2S-AgI composite was removed and Ag_2S-Ag SCN composite was applied to the membrane surface. After plane polishing and washing, the electrode was tested for its response to SCN ions in solution in the concentration range 10^{-5} to 10^{-11} M in 0.5 M $NaNO_3$ background. The results are given in Table 4.

Table-4

Concentration of SCN^- ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-5}	168.5
10^{-4}	107.4
10^{-3}	46.0
10^{-2}	-15.3
10^{-1}	-76.4

(b) As Voltammetric electrode:

The thin layer of composite active material applied earlier for

tesing as ion sensitive electrode as illustrated in example (a) above was removed by polishing on a rough emery paper and outer graphite membrane surface of the electrode was polished with successively finer grades of emergy starting from 1/0 to 5/0, to obtain a smooth membrane surface. After through washing with double distilled water the electrode was immersed in a H typo all glass voltammetric cell containing 10^{-3}M potassium ferricyanide solution in 1.0M KCI background. A platinum foil and double junction Ag/AgC1 electrodes served as counter and reference electrodes respectively. After deaeration with pure N_2 gas to remove the dissolved 0_2 present in test solution, linear sweep voltammograms (LSV) were recorded in the potential range of 1.0- 1.2 volts at potential scan rates of 50,100 and 200 mv/sec. The three LSVs are shown in Figs. 2 and 3. Fig.2 indicates linear sweep voltammograms for the graphite sensor in 10^{-3} M ferricyanide in 1M XCl at (1) 50mv/sec (2) 100mv/sec & 3) 200mv/sec. Fig 3 indicates linear sweep voltammograms for the graphite sensor at 100 mv/sec Scanrate in (a) 10^{-3}M ferricyanide in 1M KCL, (b) $5x10^{-3}$M ferricyanide in M KCL, (c) in 1M KCL background It is seen from the figure that the characteristic peak currents corresponding to the reduction of ferricyanide are observed in the LSVs and the peak current is found to increase with increasing sweep rate.

Example-2

One gramme pure graphite was homogenized with 0.3.gramme of room temperature curing silicone binder by mixing throughly in an agate mortar. The homogenized mixture was compressed in a die at

3.0 tons/cm^2 pressure for 30 minutes to obtain a substantially impervious membrane of graphite. The membrane was moulded in acetonitrile butadience styrene polymer after mixing a shielded copper wire to the inner surface of the membrane with the help of a conducting epoxy.

a) As voltammetric electrode

The outer surface of the surface of the graphite membrane of the electrode was polished with successive finer grades of emery starting from 1/0 to 5/0. After washing throughly with double distilled water, the electrode was immersed in the voltammetric cell containing 10^{-3} M potassium ferricyanide solution in 1.0 M KC1 background. After deaeration of the test solution with pure N_2 gas to remove dissolved oxygen, the LSVs were recorded with this electrode as working electrode at 100 mV/sec. potential scan rate in the potential range 1.0 to -1.0 V (curve 'a' in Fig. 3. Similar LSVs were recorded in 5 x 10^{-3} M ferricyanide in 1.0 M KCl background solution alone (curve c in Fig. 3. It is seen from the figure that the characteristic peak currents which increase with increasing ferricyanide concentration are obtained.

b) As Ion-Selective Electrode

The electrode was polished with 2/0 emergy paper and washed throughly with double distilled water. A thin coating of Ag_2S-AgB2 composite was then applied to the graphite membrane surface by rubbing. After removing loose precipitate particles by paper polishing and through washing with double distilled, water, the electrode was immersed in solutions containing bromide ions in the concentration range 10^{-6} to 10^{-1}M in 0.5 M $NaNO_3$ background.

The potential of the electrode was measured against the double junction Ag/AgCl reference electrode. The electrode potential corresponding to Br^- on concentration in solution is given below in Table 5.

Table-5

Concentration of Br^- ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	358.1
10^{-5}	314.5
10^{-4}	258.5
10^{-3}	199.5
10^{-2}	142.9
10^{-1}	82.2

After removing the Ag_2S/AgBr coating by polishing with a rough emergy, the electrode surface was polished with 2/0 emergy and a thin coating of calomel was applied. Loose particles were romoved by paper polishing and through washing with double distilled water. The electrode was then immersed in solutions containing Cl^- ions in solution in the concentration range 10^{-5} to 10^{-1} M in 0.5 M $NaNO_3$ background. The potential of the electrode corresponding to the concentration of Cl^- ions in solution are given in Table -6.

Table-6

Concentration of Cl^- ions in test solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-5}	270.0
10^{-4}	231.1
10^{-3}	176.9
10^{-2}	120.0
10^{-1}	62.0

The calomel film was removed from the membrane surface by polishing and a thin film of PbS-Ag_2S composite was applied. After paper polishing and washing with conductivity water, the elecrode was tested for its response to Pb^{2+} ions in solution in the concentration range 10^{-6} to 10^{-1} M in 0.5 M $NaNO_3$ background. The results are given in Table 7.

Table-7

Concentration of Pb^{2+} ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	-8.0
10^{-5}	4.8
10^{-4}	34.2
10^{-3}	66.1
10^{-2}	97.3
10^{-1}	128.4

After removing the PbS-Ag2Scomposite a thin layer of calomelwas applied to themembrane surface again and after paper polishing and conductivity water washing to remove loose particles. The

electrode was tested for its response to Hg^{2+} ions in solution in the concentration range 10^{-6} to 10^{-2}M in 0.5 M $NaNO_3$ background. The results are given in Table 8.

Table-8

Concentration of Hg^{2+} ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	330.2
10^{-5}	346.3
10^{-4}	379.7
10^{-3}	413.4
10^{-2}	445.6

The following are among the main advantages of the invention:

1. The graphite substrate sensor described in the present invention enables the direct estimation of a variety of cations and nions present in solution based on simple potentiometric measurements after applying appropriate active material on the surace of the sensor.

2. The same sensor as described above can be used for the determinationof different cations and anions present either in the same sample solution or different sample solutions by a simple treatment of the surface and application of a suitable active material.

3. The level of determination for a given ion present in solution using the sensor described above covers a wide range of concentrations, as illustrated in Examples 1a and 2b.

4. The same sensor described in this invention can also be used as a working electrode for voltammetric applications, as illustrated in Example 1b and 2a.

5. The sensor described above can also be used as a working electrode for amperometric applications.

Dated this 6th day of Sept. 1984

(SHUSHIL KUMAR)
ASSISTANT PATENT OFFICER
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

162241

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

"A METHOD OF MAKING A SENSOR FOR MULTI ION SENSITIVE ELECTRODE AND VOLTAMMETRIC APPLICATIONS AND THE SENSOR SO MADE".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi 110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

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This is an invention by Gollakota Prabhakar Rao, Navin Chandra, and Ganesa Ganapadigal Subramanian, Scientists of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all of them Indian Citizens and relates to a sensor for ... as ion-sensitive electrode as well as voltammetric electrode.

The graphite sensor is useful in any analytical laboratory of research and development organisation or process chemical industries where the determination of many species or ions of a variety of samples is to be carried out. The sensor will also be used in such laboratories or industries where the nature and properties of several species or constituents of such samples are to been studied by voltammetric methods. The invention relates to the multipurpose graphite substrate sensor for a variety of ion-selective electrode applications and voltametric studies.

Hitherto the concentration/activity of ions present in solutions were measured by a number of simple and direct electro-analytical methods including potentiometry. The applicability of conventional potentiometric methods is restircted to a large extent on the nonavailability of suitable indicator electrodes and/or their succeptibility to oxidation. The advent of ion-sensitive electrodes (ISE) have made possible the potentiometric analysis in redox media also. However, an ISE can be used to monitor only the ions to which the electrode is sensitive and a completely different ISE is required to measure the concentration of respective individual ions.

The object of the invention is therefore to work out the details of the procedure for making the graphite substrate sensor membrane and assemble electrodes using these membranes which when sensitized with suitable active material would give steady and stable potentials, in solutions containing corresponding ions in solution and which can also be used as voltammetric electrode.

Thus the graphite sensor of the present invention has resulted for the first time in a single gadget which serves the purpose of ISE for a host of different individual cations and anions as well as that of a working electrode for various voltammetric applications, thereby obviating/eliminating large capital investments on different individual ISE's and voltammetric electrodes.

The graphite sensor of the present invention however can be used to measure the concentration of a variety of ionic species in solution simply by the application of suitable active material on the graphite surface. The graphite surface can be very easily modified to the determination of a different ion by removing the material applied earlier by simple treatment procedures and applying a suitable different sensitising material. Another important application of the sensor is that the polished surface of graphite (without any active material applied to it) can function as a working electrode for the various voltammetric studies.

The graphite sensor is prepared by making a suitably impervious membrane by the compression of homogeneous mixture of pure

graphite powder with an inert binder and housing the membrane in a suitable holder of inert material with necessary electrical contact.

For preparation of the membrane, highly pure graphite powder is mixed thoroughly with room temperature cured silicone binder to obtain a homogeneous mixture and the mixture is compressed in a die. The membranes so obtained are mounted in hollow glass tubes with the help of an epoxy or moulded in acetonitrile butediene styrene (ABS) plastic. A shielded copper wire is fixed to the inner surface of the graphite membrane for providing electrical contact with the help of a conducting epoxy.

Accordingly the invention provides a process for making a multi ion sensitive electrode and voltametric application comprising forming a base membrane by compressing a mixture of pure graphite and a room temperature cooled silicon incorporating the membrane inside an electrode body which acts as a support for the membrane, sealing the membrane with the body using an epoxy sealant and fixing a cable to the membrane through an epoxy or moulded in acetonitrile butadiene styrene plastic.

According to a feature of this invention 0.8 to 1.0 gramme of the graphite powder is mixed with 0.2 to 0.3 gramme of the binder. The mixture obtained is compressed in a die at 3.0 to 4.5 ton/cm^2 for about 20-30 minutes. The membranes thus formed are mounted in a 15 cms length and 10 mm inner diameter hollow glass tubes.

In figure 1 of the drawings accompanying the specification a cross sectional view of an embodiment of the graphite sensor according to this invention. The sensor consists of an

impervious membrane (1) 10 mm in diameter and 6-8mm thick mounted in a solid polymeric body (2) injection moulded with ABS plastic (or fixed in a hollow glass tube with suitable adhesives) with a shield cable (3) soldered to the inner surface of the membrane with conducting epoxy (4) serving as electrical lead.

For using this membrane as ion sensitive electrode, the outer surface of the graphite membrane was polished and after washing with water, a thin coating of active material, sensitive to the ion to be estimated in solution was mechanically applied. The active material is selected from $CuS-Ag_2S$ for Cu^{2+} ions or Ag_2S-AgI for I^- ions and the like. The polishing may preferably be done using 2/0 fine emery paper. After washing the electrode was immersed in the solution of the ion of interest. The potential of the electrode was recorded against a standard reference electrode such as Ag/AgCl electrode on a pH.mV meter having a sensitivity of $\pm$ 0.1 mV. The potential of the electrode was found to bear a Nrnstian relationship with concentration of ion being detected in solution. Potential VS concentration plates are indicates in fig.2 of the drawings accompanying the provisional Specification. The line has a slope value of RT/ZF where 'Z' is the valency of the ion being estimated; R, T and F have their usual meaning.

Similarly, for voltammetric applications, the membrane was polished and linear sweep voltammograms were recorded in ferricyanide solutions in 1.0M KCl background. The polishing may preferably be done using 5% emery paper.

The following examples illustrate the various details for making

the graphite substrate sensor which are not to be considered as limiting the scope of this invention.

Example-1

0.8 gramme of pure graphite powder was throughly mixed with 0.2 gramme of room temperature curing silicone polymer in an agate mortar and tha homogenized paste was compressed in a die at 4.5 tons/cm^2 pressure for 20 minutes to obtain substantially imprevious 10 mm diameter graphite pellet. The pellet was incorporated in a glass sleeve with the help of epoxy adhesive after fixing a shielded copper wiere to the inner side of the graphite membrane with a conducting epoxy.

(a) As Ion-sensitive electrode

For ion-sensitive applications, the response of the electrode was measured for silver, cupric, iodide and thiocyanate ions in sample solutions. The experimental details are given below;

The electrode was washed several times with double distilled water after polishing the outer graphite membrane surface with 2/0 fine emery paper and Ag_2S powder was rubbed over the surface. To remove loose powder particles, the electrode was polished gently on a plane paper and washed with double distilled water. The electrode was then immersed in solutions containing silver ions in the concentration range 10^{-6} kto 10^{-1} M in 0.5 M $NaNO_3$ background and the potential of the electrode was noted down against a doubleenjunction Ag/AgCl reference electrode. The results are given below in Table -1.

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Table-1

Concentration of Ag^+ ion in solution (M)	Electrode potential (mv) vs. Ag/AgCl reference electrode
10^{-6}	235.9
10^{-5}	296.8
10^{-4}	354.3
10^{-3}	414.4
10^{-2}	473.4
10^{-1}	532.3

The Ag_2S precipitate was removed from the membrane surface by rubbing with 2/0 emery paper and Ag_2S ~ CuS composite was applied on to the membrane surface following the procedure given earlier. The loose particles of the active material were removed by gently polishing the membrane surface on a plane paper and washin under a jet of double distilled water. The electrode was then tested for its response to Cu^{2+} ions in solution in the concentration range 10^{-6} to 10^{-1} M in 0.3 M $NaNO_3$ background. The results are given in Table 2.

Table-2

Concentration of Cu^{2+} ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	216.3
10^{-5}	224.5
10^{-4}	245.5
10^{-3}	272.2
10^{-2}	300.9
10^{-1}	328.2

The CuS-Ag_2S composite was removed from the membrane surface by polishing and Ag_2S-AgI composite was applied to the membrane surface following the procedure given earlier. After removing loose precipitate and washing with double distilled water, its response was measured in solutions of iodide ions in the concentration range 10^{-6} to 10^{-1} M in 0.5 M $NaNO_3$ background. The potential of the electrode in corresponding iodide ion solutions is given in Table 3.

Table-3

Concentration of I^- ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	15.3
10^{-5}	-30.0
10^{-4}	-94.4
10^{-3}	-157.9
10^{-2}	-217.0
10^{-1}	-277.1

Following the procedure given above the Ag_2S-AgI composite was removed and Ag_2S-Ag SCN composite was applied to the membrane surface. After plane polishing and washing, the electrode was tested for its response to SCN ions in solution in the concentration range 10^{-5} to 10^{-1} M in 0.5 M $NaNO_3$ background. The results are given in Table 4.

Table-4

Concentration of SCN^- ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-5}	168.5
10^{-4}	107.4
10^{-3}	46.0
10^{-2}	-15.3
10^{-1}	-76.4

(b) As Voltammetric electrode:

The thin layer of composite active material applied earlier for testing as ion sensitive electrode as illustrated in example (a) above was removed by polishing on a rough emery paper and outer graphite membrane surface of the electrode was polished with successively finer grades of emergy starting from 1/0 to 5/0, to obtain a smooth membrane surface. After thorough washing with double distilled water the electrode was immersed in a H type all glass voltammetric cell containing 10^{-3}M potassium ferricyanide solution in 1.0M KCl background. A platinum foil and double junction Ag/AgCl electrode served as counter and reference electrodes respectively. After deaeration with pure N_2 gas to remove the dissolved O_2 present in test solution, linear sweep voltammograms (LSV) were recorded in the potential range of 1.0- 1.2 volts at potential scan rates of 50, 100 and 200 mv/sec. The three LSVs are shown in Fig. 1 of the drawings accompanying the present Specification. It is seen from the figure that the characteristic eak currents corresponding to the reduction of ferricyanide are observed in the LSVs and the peak current is found to increase with increasing sweep rate.

Example-2

One gramme pure graphite was homogenized with 0.3 gramme of room temperature curing silicone binder by mixing throughly in an agate mortar. The Homogenized mixture was compressed in a dic at 3.0 tons/cm^2 pressure for 30 minutes to obtain a substantially impervious membrane of graphite. The membrane was moulded in acetonitrile butadiene styrene polymer after fixing a shielded copper wire to the inner surface of the membrane with the help of a conducting epoxy.

a) As voltammetric electrode

The outer surface of the graphite membrane of the electrode was polished with successive finer grades of emery starting from 1/0 to 5/0. After washing throughly with double distilled water, the electrode was immersed in the voltammetric cell containing 10^{-3} M potassium ferricyanide solution in 1.0 M KCl background. After deaeration of the test solution with pure N_2 gas to remove dissolved oxygen, the LSVs were recorded with this electrode as working electrode at 100 mV/sec. potential scan rate in the potential range 1.0 to -1.0 V (curve 'a' in Fig. 3. Similar LSVs were recorded in 5 x 10^{-3} M ferricyanide in 1.0 M KCl background solution alone (curve c in Fig.2 of sheet 2). It is seen from the figure that the characteristic peak currents which increase with increasing ferricyanide concentration are obtained.

b) As Ion-Selective Electrode

The electrode was polished with 2/0 emergy paper and washed throughly with double distilled water. A thin coating of Ag_2S-

AgBr composite was then applied to the graphite membrane surface by rubbing. After removing loose precipitate particles by paper polishing and thorough washing with double distilled, water, the electrode was immersed in solutions containing bromide ions in the concentration range 10^{-6} to 10^{-1}M in 0.5 M $NaNO_3$ background. The potential of the electrode was measured against the double junction Ag/AgCl reference electrode. The electrode potential corresponding to Br ion concentration in solution is given below in Table-5.

Table-5

Concentration of Br ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	358.1
10^{-5}	314.5
10^{-4}	258.5
10^{-3}	199.5
10^{-2}	142.9
10^{-1}	82.2

After removing the Ag_2S/AgBr coating by polishing with a rough emergy, the electrode surface was polished with 2/0 emergy and a thin coating of calomel was applied. Loose particles were romoved by paper polishing and thorough washing with double distilled water. The electrode was then immersed in solutions containing Cl^- ions in solution in the concentration range 10^{-5} to 10^{-1} M in 0.5 M $NaNO_3$ background. The potential of the electrode corresponding to the concentration of Cl^- ions in solution are given in Table -6.

Table-6

Concentration of Cl^- ions in test solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-5}	270.0
10^{-4}	231.1
10^{-3}	176.9
10^{-2}	120.0
10^{-1}	62.0

The calomel film was removed from the membrane surface by polishing and a thin film of PbS-Ag_2S composite was applied. After paper polishing and washing with conductivity water, the elecrode was tested for its response to Pb^{2+} ions in solution in the concentration range 10^{-6} to 10^{-1} M in 0.5 M $NaNO_3$ background. The results are given in Table 7.

Table-7

Concentration of Pb^{2+} ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	-8.0
10^{-5}	4.8
10^{-4}	34.2
10^{-3}	66.1
10^{-2}	97.3
10^{-1}	128.4

After removing the PbS-Ag2Scomposite a thin layer of calomel was applied to the membrane surface again and after paper polishing and conductivity water washing to remove loose particles. The

electrode was tested for its response to Hg^{2+} ions in solution in the concentration range 10^{-6} to 10^{-2}M in 0.5 M $NaNO_3$ background. The results are given in Table 8.

Table-8

Concentration of Hg^{2+} ions in solution (M)	Electrode potential (mV) vs Ag/AgCl reference electrode
10^{-6}	330.2
10^{-5}	346.3
10^{-4}	379.7
10^{-3}	413.4
10^{-2}	445.6

The following are among the main advantages of the invention:

1. The graphite substrate sensor described in the present invention enables the direct estimation of a variety of cations and anions present in solution based on simple potentiometric measurements after applying appropriate active material on the surface of the sensor.

2. The same sensor as described above can be used for the determinationof different cations and anions present either in the same sample solution or different sample solutions by a simple treatment of the surface and application of a suitable active material.

3. The level of determination for a given ion present in solution using the sensor described above covers a wide range of concentrations.

4. The same sensor described in this invention can also be used as a working electrode for voltametric applications.

5. The sensor described above can also be used as a working electrode for amperometric applications.

WE CLAIM

162241

1. A method for making a sensor for multi ion sensitive electrode and voltametric application comprising forming a base membrane by compressing a mixture of pure graphite and a room temperature cooled silicone, incorporating the membrane inside an electrode body which acts as a support for the membrane, sealing the membrane with the body using an epoxy sealant and fixing a cable to the membrane through an epoxy or moulded in an acetonitrile butadiene styrene plastic.

2. A method as claimed in claim 1 wherein the compression is done in a die at 3.0 to 4.5 ton/cm^2 for 20-30 minutes.

3. A sensor for multi ion sensitive electrode and voltametric application made according to the method as claimed in claims 1 and 2.

4. A method for making a sensor for multi ion sensitive electrode and voltameter application substantially as herein described with reference to the examples and the drawings accompanying this specification.

Dated this 4th day of December 1985

(N.R. SUBBARAM)
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COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

Nº. OF SHEETS - 1

SHEET Nº - 1

App No. 709/DEL/64

COMPLETE SPECIFICATION

162241

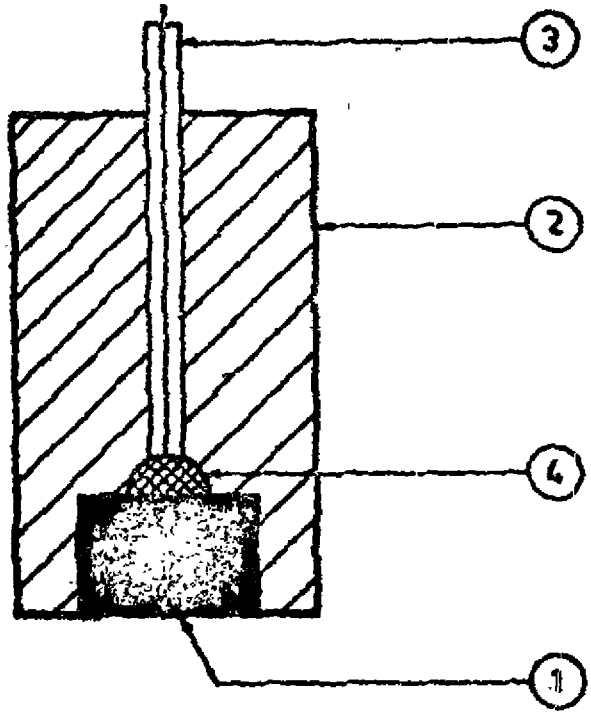

FIG. 1

N. R. Srikaran

T.M.S.

PATENTS OFFICER,

C.S.I.R.